

PATENT ABSTRACTS OF JAPAN

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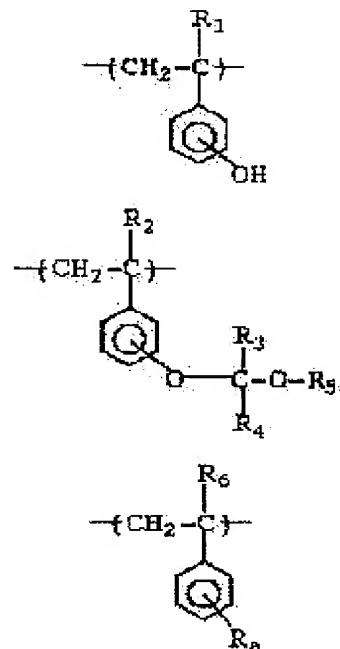
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(54) RADIATION SENSITIVE COMPOSITION



(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a chemically sensitizable positive resist effectively responsive to various kinds of radiations including ultraviolet rays, etc., and superior in sensitivity and resolution and developability and a pattern form and to enhance the storage stability of sensitivity by incorporating a copolymer comprising various kinds of specified repeating units and a radiation sensitive acid generator.

SOLUTION: The radiation sensitive composition contains the copolymer comprising the repeating units represented by formula I and those represented by formula II and the copolymer comprising those represented by formula III and formula I and a radiation sensitive acid generator, and in formulae I-III, each of R_1 and R_2 is an H atom or a methyl group; R_3 is an H atom or a 1-10C chain or cyclic alkyl group or the like; each of R_4 and R_5 is, independently, a 1-10C chain alkyl or 1-10C alkylhalide group or the like; R_6 is an H atom or a

group; R_3 is an H atom or a 1-10C chain or cyclic alkyl group or the like; each of R_4 and R_5 is, independently, a 1-10C chain alkyl or 1-10C alkylhalide group or the like; R_6 is an H atom or a

methyl group; and Ra is an H atom or a 1-10C alkyl group.

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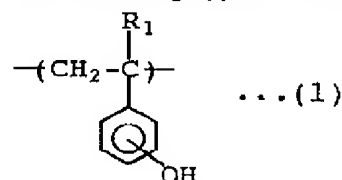
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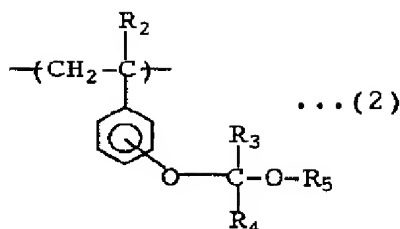
CLAIMS

[Claim(s)]

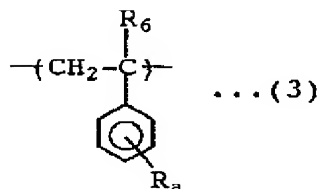
[Claim 1] (A) The copolymer, [Formula 1] which come to contain the repeating unit expressed with the following type (1), and the repeating unit expressed with the following type (2)



Here, R1 is [Formula 2] which shows a hydrogen atom or a methyl group.



R2 shows a hydrogen atom or a methyl group here. R3 A hydrogen atom, the chain-like alkyl group of carbon numbers 1-10, The aryl group of the annular alkyl group of carbon numbers 3-10 and carbon numbers 6-10 or the aralkyl radical of carbon numbers 7-11 is shown. R4 and R5 mutually-independent The chain-like alkyl group of carbon numbers 1-10, the alkyl halide radical of carbon numbers 1-10, The aryl group of the annular alkyl group of carbon numbers 3-10 and carbon numbers 6-10 or the aralkyl radical of carbon numbers 7-11 is shown, or R3, R4, and R5 may join together mutually [any two], and five to 7 membered-ring may be formed. (B) Copolymer which comes to contain the repeating unit expressed with the repeating unit and the above-mentioned formula (1) which are expressed with the following formula (3) [** 3]



It is the radiation-sensitive constituent which R6 shows a hydrogen atom or a methyl group, and Ra shows a hydrogen atom or the alkyl group of carbon numbers 1-10 here, and is characterized by containing (C) radiation-sensitive acid generator.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a radiation-sensitive constituent. It is related with a radiation-sensitive constituent useful as a resist suitable in more detail for micro processing which uses the various radiations like ultraviolet rays, far ultraviolet rays, an X-ray, or a charged-particle line.

[0002]

[Description of the Prior Art] In the field of micro processing represented by manufacture of an integrated circuit device, in order to obtain the higher degree of integration of an integrated circuit, detailed-ization of the design rule in lithography is advancing quickly, and development of the lithography process which is stabilized and can perform micro processing of high degree of accuracy with a line breadth of 0.5 micrometers or less is strongly promoted in recent years. However, by the

approach using a conventional visible ray (wavelength of 700–400nm) and a conventional near ultraviolet ray (wavelength of 400–300nm), the depth of focus with broader difficult therefore forming such a detailed pattern in high degree of accuracy can be attained, and the lithography process using the radiation of short wavelength (wavelength of 300nm or less) effective in detailed-izing of a design rule is proposed.

[0003] As a lithography process using the radiation of such short wavelength, the approach of using charged-particle lines, such as X-rays, such as far ultraviolet rays, such as a KrF excimer laser (wavelength of 248nm) and an ArF excimer laser (wavelength of 193nm), and a synchrotron radiation line, or an electron ray, for example is proposed. And as a high resolution resist corresponding to the radiation of these short wavelength, a "chemistry magnification mold resist" is advocated by the International business machine (IBM) company, and amelioration of current and this chemistry magnification mold resist is advanced energetically.

[0004] Such a chemistry magnification mold resist generates an acid by the exposure (henceforth "exposure") of the radiation to the radiation-sensitive acid generator which it is made to contain, by the catalysis of this acid, in the resist film, chemical reactions (for example, a polar change, decomposition of a chemical bond, crosslinking reaction, etc.) are made to occur, and the solubility over a developer forms a pattern using the phenomenon of change in the exposure section.

[0005] To and the thing which shows the comparatively good resist engine performance among the conventional chemistry magnification mold resists The resin which protected the alkali compatibility radical in alkali fusibility resin by t-butyl ester group or the t-butoxycarbonyl group as a resinous principle (refer to JP,2-27660,B), As the resin (refer to JP,3-44290,B) which protected the alkali compatibility radical in alkali fusibility resin by the silyl radical, and a resinous principle The resist which used the resin (refer to JP,7-140666,A) which protected the alkali compatibility radical in alkali fusibility resin by the ketal radical, and the resin (refer to JP,2-161436,A and JP,5-249682,A) protected by the acetal radical is known.

[0006] However, there is a problem of a proper in these chemistry magnification mold resists, respectively, and being accompanied by various difficulties on the occasion of utilization is pointed out.

[0007] The line breadth of a resist pattern changes or becoming T-mold configuration as the big problem by the length soaking time (Post Exposure Time Delay it being called "PED" below.) from exposure to postbake is mentioned. The approach (JP,8-15864,A) of blending the resin protected by the acetal radical as a means to solve these problems, and the resin protected by the t-butoxycarbonyl group is proposed, and it is known that the comparatively good resist engine performance is shown. However, when it considered as a resist solution and the thing of this combination saved this, it had the problem that sensibility changed. Moreover, a pattern configuration, sensibility, development nature, and resolution are also inadequate, and the further improvement is called for from a viewpoint of the overall characteristic as a chemistry magnification mold resist.

[0008]

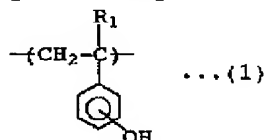
[Problem(s) to be Solved by the Invention] The object of this invention is to offer a

radiation-sensitive constituent useful as a chemistry magnification mold positive resist which responded effective in ultraviolet rays, far ultraviolet rays, an X-ray, or the various radiations like an electrification meridian, was excellent in sensibility, resolution, development nature, and a pattern configuration, and was moreover excellent in the preservation stability of sensibility.

[0009]

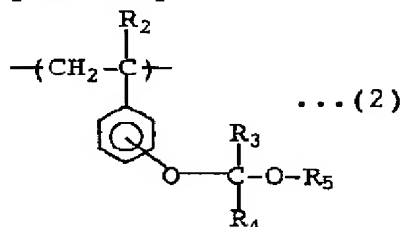
[Means for Solving the Problem] According to this invention, said object is the copolymer (henceforth "a copolymer (A)") which comes to contain the repeating unit expressed with the (A) following type (1), and the repeating unit expressed with the following type (2), and [0010].

[Formula 4]



[0011] Here, R₁ is [0012] which shows a hydrogen atom or a methyl group.

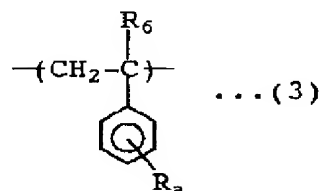
[Formula 5]



[0013] R₂ shows a hydrogen atom or a methyl group here. R₃ The chain-like alkyl group of the hydrogen atom carbon numbers 1-10, The aryl group of the annular alkyl group of carbon numbers 3-10 and carbon numbers 6-10 or the aralkyl radical of carbon numbers 7-11 is shown. R₄ and R₅ mutually-independent The chain-like alkyl group of carbon numbers 1-10, the alkyl halide radical of carbon numbers 1-10, The aryl group of the annular alkyl group of carbon numbers 3-10 and carbon numbers 6-10 or the aralkyl radical of carbon numbers 7-11 is shown, or R₃, R₄, and R₅ may join together mutually [any two], and five to 7 membered-ring may be formed. (B) Copolymer which consists of a repeating unit expressed with the repeating unit and the above-mentioned formula (1) which are expressed with the following formula (3) (henceforth "a copolymer (B)")

[0014]

[Formula 6]



[0015] Here, R₆ shows a hydrogen atom or a methyl group, and it is attained by the radiation-sensitive and constituent which R_a shows a hydrogen atom or the alkyl group of carbon

numbers 1-10, and is characterized by containing (C) radiation-sensitive acid generator. Hereafter, although this invention is explained to a detail, thereby, the object, the configuration, and effectiveness of this invention will become clear.

[0016] The copolymer (A) used in copolymer (A) this invention is a copolymer expressed with the repeating unit (henceforth "a repeating unit (1)") expressed with said formula (1), and the repeating unit (henceforth "a repeating unit (2)") expressed with said formula (2). In a formula (1), R1 is a hydrogen atom or a methyl group. In a formula (2), R2 is a hydrogen atom or a methyl group. Moreover, R3 is the aryl group of a hydrogen atom, the chain-like alkyl group of carbon numbers 1-10 (C1-C10), the annular alkyl group of carbon numbers 3-10 (C3-C10), and carbon numbers 6-10 (C6-C10), or the aralkyl radical of carbon numbers 7-11 (C7-C11).

[0017] The chain-like alkyl group of C1-C10 may be a straight chain-like, may be branched-chain, for example, can mention a methyl group, an ethyl group, n-propyl group, i-propyl group, n-butyl, i-butyl, sec-butyl, t-butyl, n-pentyl radical, a neopentyl radical, n-hexyl group, n-heptyl radical, n-octyl radical, a 2-ethylhexyl radical, n-nonyl radical, n-decyl group, etc.

[0018] As an annular alkyl group of C3-C10, a cyclo propyl group, cyclo butyl, a cyclopentyl group, a cyclohexyl radical, a cycloheptyl radical, a cyclo octyl radical, a norbornyl radical, an isobornyl radical, etc. can be mentioned, for example.

[0019] As an aryl group of C6-C10, a phenyl group, a tolyl group, a xylyl group, a KUMENIRU radical, 1-naphthyl group, etc. can be mentioned, for example.

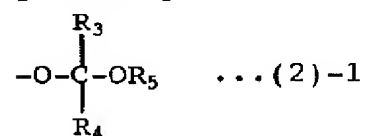
[0020] Moreover, as an aralkyl radical of C7-C11, benzyl, alpha-methylbenzyl radical, a phenethyl radical, a naphthyl methyl group, etc. can be mentioned, for example.

[0021] Furthermore, R4 and R5 are the aryl group of the alkyl group of the shape of C1 - C10 chain, the alkyl halide radical of C1-C10, the annular alkyl group of C3-C10, and C6-C10, or the aralkyl radical of C7-C11 mutually-independent in a formula (2). The thing same [among these] as an example of radicals other than an alkyl halide radical as the above mentioned thing can be mentioned, and a trifluoroethyl radical, a hexafluoro propyl group, a heptadeca fluoro decyl group, etc. can be mentioned as alkyl halide, for example.

[0022] Moreover, it can join together mutually and R3, R4, and R5 can form five to 7 membered-ring. As five to 7 membered-ring when R3 and R4 join together, a cyclopentyl group, a cyclohexyl radical, and a cycloheptyl radical can be mentioned, for example. Moreover, as five to 7 membered-ring when R3, R5, or R4 and R5 join together, a tetrahydrofuranyl radical and a tetrahydropyranyl group can be mentioned, for example.

[0023] Following type (2)-1 [0024] [in / a deer is carried out and / the above-mentioned formula (2)]

[Formula 7]



[0025] the radical as the above-mentioned formula (2) with the same definition of R3, R4, and R5

come out of and expressed is a radical called an acetal radical or a ketal radical here. As an acetal radical, here, for example A 1-methoxyethoxy radical, a 1-ethoxy ethoxy radical, A 1-n-propoxyethoxy radical, a 1-i-propoxyethoxy radical, a 1-n-butoxyethoxy radical, A 1-i-butoxyethoxy radical, a 1-sec-butoxyethoxy radical, a 1-t-butoxyethoxy radical, 1-cyclopentyl oxyethoxy radical, 1-cyclohexyl oxyethoxy radical, 1-norbornyl oxyethoxy radical, a 1-bornyl oxyethoxy radical, 1-phenyloxy ethoxy radical, a 1-(1-naphthyloxy) ethoxy radical, A 1-benzyloxy ethoxy radical, 1-phenethyl oxyethoxy radical, A methoxy group, a methoxy group (ethoxy (cyclohexyl)), (Cyclohexyl) (methoxy) A methoxy group, a methoxy group (i(cyclohexyl)-propoxy), (Cyclohexyl) (n-propoxy) A methoxy group, a methoxy group (phenoxy (cyclohexyl)), (Cyclohexyl) (cyclohexyloxy) A methoxy group, a methoxy group (methoxy (phenyl)), (Cyclohexyl) (benzyloxy) A methoxy group, a methoxy group (n(phenyl)-propoxy), (Phenyl) (ethoxy) A methoxy group, a methoxy group (cyclohexyloxy (phenyl)), (Phenyl) (i-propoxy) A methoxy group, a methoxy group (benzyloxy (phenyl)), (Phenyl) (phenoxy) A methoxy group, a methoxy group (ethoxy (benzyl)), (Benzyl) (methoxy) A methoxy group, a methoxy group (i(benzyl)-propoxy), (Benzyl) (n-propoxy) (Benzyl) A methoxy group, a methoxy group (phenoxy (benzyl)), a methoxy group (benzyloxy (benzyl)), a 2-tetrahydrofuranyl oxy-radical, 2-tetrahydropyranyloxy radical, etc. can be mentioned (cyclohexyloxy).

[0026] As a ketal radical, for example Next, a 1-methyl-1-methoxyethoxy radical, A 1-methyl-1-ethoxy ethoxy radical, a 1-methyl-1-n-propoxyethoxy radical, A 1-methyl-1-i-propoxyethoxy radical, a 1-methyl-1-n-butoxyethoxy radical, A 1-methyl-1-i-butoxyethoxy radical, a 1-methyl-1-sec-butoxyethoxy radical, A 1-methyl-1-t-butoxyethoxy radical, a 1-methyl-1-cyclopentyl oxyethoxy radical, A 1-methyl-1-cyclohexyl oxyethoxy radical, a 1-methyl-1-norbornyl oxyethoxy radical, A 1-methyl-1-bornyl oxyethoxy radical, a 1-methyl-1-phenyloxy ethoxy radical, A 1-methyl-1-(1-naphthyloxy) ethoxy radical, a 1-methyl-1-benzyloxy ethoxy radical, A 1-methyl-1-phenethyl oxyethoxy radical, a 1-cyclohexyl-1-methoxyethoxy radical, A 1-cyclohexyl-1-ethoxy ethoxy radical, a 1-cyclohexyl-1-n-propoxyethoxy radical, A 1-cyclohexyl-1-i-propoxyethoxy radical, a 1-cyclohexyl-1-cyclohexyl oxyethoxy radical, A 1-cyclohexyl-1-phenoxy ethoxy radical, a 1-cyclohexyl-1-benzyloxy ethoxy radical, A 1-phenyl-1-methoxyethoxy radical, a 1-phenyl-1-ethoxy ethoxy radical, A 1-phenyl-1-n-propoxyethoxy radical, a 1-phenyl-1-i-propoxyethoxy radical, A 1-phenyl-1-cyclohexyl oxyethoxy radical, a 1-phenyl-1-phenyloxy ethoxy radical, A 1-phenyl-1-benzyloxy ethoxy radical, a 1-benzyl-1-methoxyethoxy radical, A 1-benzyl-1-ethoxy ethoxy radical, a 1-benzyl-1-n-propoxyethoxy radical, A 1-benzyl-1-i-propoxyethoxy radical, a 1-benzyl-1-cyclohexyl oxyethoxy radical, A 1-benzyl-1-phenyloxy ethoxy radical, a 1-benzyl-1-benzyloxy ethoxy radical, A 2-(2-methyl-tetrahydrofuranyl) oxy-radical, a 2-(2-methyl-tetrahydropyranyl) oxy-radical, a 1-methoxy-cyclopenthyloxy radical, a 1-methoxy-cyclohexyloxy radical, etc. can be mentioned.

[0027] (A) In a copolymer, a repeating unit (1) and (2) can be independent, or they can exist two or more sorts. (A) — the content of the repeating unit (2) in a copolymer — a repeating unit (1) and

criteria [sum total / of (2)] -- carrying out -- 10 - 60-mol % -- desirable -- 20 - 50-mol % -- it is 25 - 45-mol % still more preferably. Less than [10 mol %], when there is an inclination for the resolution as a resist to fall and 60-mol % is exceeded on the other hand, there is an inclination for sensibility to fall.

[0028] The repeating unit (henceforth "a repeating unit (4)") of these and other copolymerizable monomers can be made to contain in a copolymer (A) in addition to a repeating unit (1) and a repeating unit (2). Copolymerization of the repeating unit (4) is carried out for improvement in a pattern configuration and resolution, and it is guided from the monomer which does not have acid hydroxyl groups, such as the soluble low monomer to an alkali developer, i.e., a sulfonic group, a carboxylic-acid radical, and a phenolic hydroxyl group. As an example of such a monomer (henceforth "a monomer (4)"), a vinyl group content compound, an acrylamide (meta) compound, and acrylic ester (meta) can be mentioned.

[0029] Here, as a vinyl group content compound, cyano group content vinyl compounds, such as hetero atom content alicyclic vinyl compound; acrylonitrile, such as aromatic series vinyl compounds, such as styrene, alpha methyl styrene, p-methyl styrene, KURORU styrene, and t-butoxy styrene, vinyl pyrrolidone, and a vinyl caprolactam, and a methacrylonitrile, are mentioned, for example. (Meta) As an acrylamide compound, acrylamide, methacrylamide, N-methylol acrylamide, etc. can be mentioned, for example.

[0030] Moreover, as acrylic ester (meta), alkyl (meta) acrylate, such as methyl (meta) acrylate and ethyl (meta) acrylate, hydroxyethyl (meta) acrylate, phenyl (meta) acrylate, isoboronyl (meta) acrylate, tricyclo deca nil acrylate, etc. can be mentioned, for example.

[0031] although the suitable content of a repeating unit (4) changes with a repeating unit (1) and operating rates of (3) -- general -- all the repeating units of a copolymer (A) -- receiving -- usually -- 0 - 30-mol % -- desirable -- 0 - 20-mol % -- it is 5 - 20-mol % still more preferably. When 40-mol % is exceeded, it is in the inclination for the solubility over a developer to fall.

[0032] The above-mentioned copolymer (A) can be manufactured by the following approach.

(b) The vinyl aromatic series system (**) polymer which has a phenolic hydroxyl group (It is hereafter called a "phenolic hydroxyl group content polymer" (p-hydroxystyrene).), for example, Pori, Pori (p-isopropenyl FENIRU) etc. is prepared. The one section of the hydroxyl group For example, make it react with ethyl vinyl ether, 2, a 3-dihdropyran, the 4-methoxy -5, a 6-dihydro-2H-pyran, or 2-methoxy propylene **** compound, and it etherifies. How to manufacture the polymer which consists of a repeating unit of said formula (1), and a repeating unit of said formula (2).

(b) How to carry out a demineralization-ized sodium reaction and to etherify the sodium-phenoxide derivative of a phenolic hydroxyl group content polymer, and the compound expressed with formula $\text{Cl-CH(R3) (R4) OR5}$ (however, R3, R4, and R5 are the same as R3, R4, and R5 in a formula (2) respectively).

(c) How to copolymerize the vinyl aromatic compound corresponding to said formula (1) and (2) directly.

[0033] In addition, the polystyrene equivalent weight average molecular weight (henceforth "Mw")

by the gel permeation chromatography (henceforth "GPC") of a copolymer (A) is usually 1,000–100,000, is 3,000–40,000 preferably, and is 3,000–30,000 still more preferably. When it considers as a resist for it to be less than 1,000 molecular weight, and sensibility and thermal resistance are easy to be inferior and 100,000 is exceeded, it becomes easy to be inferior [the solubility of the radiation irradiation section of the resist to a developer].

[0034] The copolymers (B) used in copolymer (B) this invention are the repeating unit (henceforth "a repeating unit (3)") expressed with the above-mentioned formula (3), and a copolymer which consists of a repeating unit (1). In a formula (3), R₆ is a hydrogen atom or a methyl group, and R_a is a hydrogen atom or the alkyl group of carbon numbers 1–10. As an example of the alkyl group of carbon numbers 1–10, the example of the chain-like alkyl group of the above mentioned carbon numbers 1–10 or the annular alkyl group of carbon numbers 3–10 is given.

[0035] the content of the repeating unit (1) in a copolymer (B) — usually — 50 – 95-mol % — desirable — 55 – 90-mol % — it is 60 – 80-mol % still more preferably. Less than [50 mol %], the sensibility as a resist tends to fall, and if 95-mol % is exceeded on the other hand, the inclination for whenever [development] to fall will serve as size.

[0036] the content of the repeating unit (3) in a copolymer (B) — usually — 5 – 50-mol % — desirable — 10 – 45-mol % — it is 20 – 40-mol % still more preferably. Less than [5 mol %], the resolution as a resist tends to fall, and when 50-mol % is exceeded on the other hand, it is in the inclination to become easy for development nature to fall.

[0037] The repeating unit (henceforth "a repeating unit (5)") of these and other copolymerizable monomers can be made to contain in a copolymer (B) in addition to a repeating unit (1) and a repeating unit (3). Copolymerization of the repeating unit (5) is carried out for improvement in a pattern configuration and resolution, and it is guided from the monomer which does not have acid hydroxyl groups, such as the soluble low monomer to an alkali developer, i.e., a sulfonic group, a carboxylic-acid radical, and a phenolic hydroxyl group. As an example of such a monomer (henceforth "a monomer (4)"), a vinyl group content compound, an acrylamide (meta) compound, and acrylic ester (meta) can be mentioned. Here, as a vinyl group content compound, cyano group content vinyl compounds, such as hetero atom content alicyclic vinyl compound; acrylonitrile, such as aromatic series vinyl compounds, such as KURORU styrene and t-butoxy styrene, vinyl pyrrolidone, and a vinyl caprolactam, and a methacrylonitrile, are mentioned, for example. (Meta) As an acrylamide compound, acrylamide, methacrylamide, N-methylol acrylamide, etc. can be mentioned, for example.

[0038] Moreover, as acrylic ester (meta), alkyl (meta) acrylate, such as methyl (meta) acrylate and ethyl (meta) acrylate, hydroxyethyl (meta) acrylate, phenyl (meta) acrylate, etc. can be mentioned, for example. Although the suitable content of a repeating unit (5) changes with a repeating unit (1) and operating rates of (3), generally it is usually less than [30 mol %] to all the repeating units of a copolymer (A). When 30-mol % is exceeded, it is in the inclination for the solubility over a developer to fall.

[0039] The above-mentioned copolymer (B) can be manufactured by the approach of the following (d) – (**).

(d) How to carry out direct radical copolymerization of the vinyl aromatic compound corresponding to the above-mentioned formula (1) and (3).

(e) How to hydrolyze from an acid, after copolymerizing the vinyl aromatic compound corresponding to t-butoxy styrene and the above-mentioned formula (3).

(**) How to hydrolyze with alkali, after copolymerizing the vinyl aromatic compound corresponding to acetoxy styrene and the above-mentioned formula (3).

[0040] (B) Mw(s) of a copolymer are usually 1,000–100,000, are 3,000–40,000 preferably, and are 3,000–30,000 still more preferably. When it considers as a resist for molecular weight to be less than 3,000, and sensibility and thermal resistance are easy to be inferior and 100,000 is exceeded, it becomes easy to be inferior [the solubility of the exposure line exposure section of the resist to a developer]. these copolymers (B) are independent — or it is used by two or more sorts, mixing.

[0041] this invention — setting — the operating rate of a copolymer (A) and a copolymer (B) — the weight ratio of (Copolymer A) tare coalesce (B) — 50 / 50 – 95/5 — desirable — 60 / 40 – 90/10 — it is 70 / 30 – 90/10 still more preferably. In addition, these weight ratios are the things at the time of making sum total weight of a copolymer (A) and a copolymer (B) into the 100 weight sections.

[0042] A radiation-sensitive acid generator radiation-sensitive acid generator is a compound which generates an acid by radiation irradiation. As a radiation-sensitive acid generator used in this invention, ** onium salt, ** sulfone compound, ** sulfonate compound, ** sulfone imide compound, etc. can be mentioned. The example of these radiation-sensitive acid generators is shown below.

[0043] ** Onium salt : as onium salt, iodonium salt, sulfonium salt, phosphonium salt, diazonium salt, ammonium salt, pyridinium salt, etc. can be mentioned, for example. As an example of an onium salt compound, diphenyliodonium trifluoromethane sulfonate, Diphenyliodonium pyrene sulfonate, diphenyliodonium dodecylbenzene sulfonate, Triphenylsulfonium trifluoromethane sulfonate, triphenyl sulfonium tosylate, Diphenyliodonium hexafluoroantimonate, triphenylsulfonium naphthalene sulfonate, Triphenylsulfonium camphor sulfonate, benzyl (hydroxyphenyl) methyl sulfonium toluenesulfonate, G (t-buthylphenyl) iodonium nonafluorobutane sulfonate, G (t-buthylphenyl) iodonium toluenesulfonate, G (t-buthylphenyl) iodonium camphor sulfonate, G (t-buthylphenyl) iodonium naphthalene sulfonate, etc. can be mentioned.

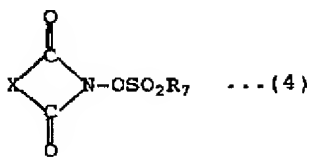
[0044] ** Sulfone compound : as a sulfone compound, a beta-keto sulfone, beta-sulfonyl sulfones, these alpha-diazo compounds, etc. can be mentioned, for example. As an example of a sulfone compound, a phenacyl phenyl sulfone, a mesityl phenacyl sulfone, bis(phenyl sulfonyl) methane, 4-tris phenacyl sulfone, etc. can be mentioned.

[0045] ** Sulfonate compound : as a sulfonate compound, an alkyl sulfonate, a halo alkyl sulfonate, an aryl sulfonate, imino sulfonate, etc. can be mentioned, for example. As an example of a sulfonate compound, benzoin tosylate, pyrogallol tris (trifluoromethane SURUHOTO), pyrogallol methansulfonic acid triester, nitrobenzyl -9, 10-diethoxy anthracene-2-sulfonate, alpha-methylol benzoin tosylate, alpha-methylol benzoin octane sulfonate, alpha-methylol benzoin trifluoro methansulfonic acid ester, alpha-methylol benzoin dodecyl sulfonate, etc. can be mentioned.

[0046] ** Sulfone imide compound : as a sulfone imide compound, it is the following type (4), for example.

[0047]

[Formula 8]



[0048] here, X shows divalent radicals, such as an alkylene group, an arylene radical, and an ARUKO xylene radical, it can come out and R7 can mention the compound in which univalent radicals, such as an alkyl group, an aryl group, a halogenation alkyl group, and a halogenation aryl group, are shown and which is expressed.

[0049] As an example of a sulfone imide compound, N-(trifluoromethyl sulfonyloxy)succinimide, N-(trifluoromethyl sulfonyloxy)phthalimide, N-(trifluoromethyl sulfonyloxy) diphenyl maleimide, The N-(trifluoromethyl sulfonyloxy) bicyclo [2.2.1] hept-5-en -2, 3-dicarboxyimide, The N-(trifluoromethyl sulfonyloxy)-7-OKISA bicyclo [2.2.1] hept-5-en -2, 3-dicarboxyimide, N-(trifluoromethyl sulfonyloxy) naphthyl imide, the N-(trifluoromethyl sulfonyloxy) bicyclo [2.2.1] heptane -5, 6-oxy-- 2, 3-dicarboxyimide, N-(camphor sulfonyloxy) succinimide, N-(camphor sulfonyloxy) phthalimide, N-(camphor sulfonyloxy) diphenyl maleimide, the N-(camphor sulfonyloxy) bicyclo [2.2.1] hept-5-en -2, 3-dicarboxyimide, The N-(camphor sulfonyloxy)-7-OKISA bicyclo [2.2.1] hept-5-en -2, 3-dicarboxyimide, N-(camphor sulfonyloxy) naphthyl imide, the N-(camphor sulfonyloxy) bicyclo [2.2.1] heptane -5, 6-oxy-- 2, 3-dicarboxyimide, [0050] N-(4-methylphenyl sulfonyloxy) succinimide, N-(camphor sulfonyloxy) naphthyl dicarboxyimide, N-(4-methylphenyl sulfonyloxy) phthalimide, N-(4-methylphenyl sulfonyloxy) diphenyl maleimide, The N-(4-methylphenyl sulfonyloxy) bicyclo [2.2.1] hept-5-en -2, 3-dicarboxyimide, The N-(4-methylphenyl sulfonyloxy)-7-OKISA bicyclo [2.2.1] hept-5-en -2, 3-dicarboxyimide, N-(4-methylphenyl sulfonyloxy) naphthyl imide, the N-(4-methylphenyl sulfonyloxy) bicyclo [2.2.1] heptane -5, 6-oxy-- 2, 3-dicarboxyimide, N-(2-trifluoromethyl phenylsulfonyloxy) succinimide, N-(2-trifluoromethyl phenylsulfonyloxy) phthalimide, N-(2-trifluoromethyl phenylsulfonyloxy) diphenyl maleimide, The N-(2-trifluoromethyl phenylsulfonyloxy) bicyclo [2.2.1] hept-5-en -2, 3-dicarboxyimide, The N-(2-trifluoromethyl phenylsulfonyloxy)-7-OKISA bicyclo [2.2.1] hept-5-en -2, 3-dicarboxyimide, N-(2-trifluoromethyl phenylsulfonyloxy) naphthyl imide, The N-(2-trifluoromethyl phenylsulfonyloxy) bicyclo [2.2.1] heptane -5, 6-oxy-- 2, 3-dicarboxyimide, N-(2-trifluoromethyl phenylsulfonyloxy) naphthyl imide, N-(4-fluoro phenylsulfonyloxy) succinimide, N-(2-fluoro phenyl) phthalimide, N-(4-fluoro phenylsulfonyloxy) diphenyl maleimide, The N-(4-fluoro phenylsulfonyloxy) bicyclo [2.1.1] hept-5-en -2, 3-dicarboxyimide, The N-(trifluoromethyl sulfonyloxy)-7-OKISA bicyclo [2.1.1] hept-5-en -2, 3-dicarboxyimide, The N-(4-fluoro phenylsulfonyloxy) bicyclo [2.1.1] heptane -5, 6-oxy-- 2, 3-dicarboxyimide, N-(4-fluoro phenylsulfonyloxy) naphthyl dicarboxyimide, etc. can be mentioned.

[0051] ** onium salt and ** sulfone compound are desirable among said radiation-sensitive acid generators. Especially Triphenylsulfonium trifluoromethane sulfonate, triphenylsulfonium

naphthalene sulfonate, Triphenylsulfonium camphor sulfonate, a bis(phenyl sulfonyl) cyclohexane, Bis(phenyl sulfonyl) cyclopentene, G (t-buthylphenyl) iodonium nonafluorobutane sulfonate, G (t-buthylphenyl) iodonium tosylate, G (t-buthylphenyl) iodonium camphor sulfonate, G (t-buthylphenyl) iodonium naphthalene sulfonate, etc. are desirable.

[0052] this invention -- setting -- the above-mentioned radiation-sensitive acid generator -- usually -- per a total of 100 weight sections of a copolymer (A) and a copolymer (B), and 1 - 20 weight section -- it is especially used at a rate of 1 - 10 weight section preferably. They are used for these radiation-sensitive acid generators (henceforth an "acid generator") for independent or two kinds or more, mixing.

[0053] In acid diffusion control agent this invention, it is desirable to blend the acid diffusion control agent which has the operation which controls the diffusion phenomenon in the resist coat of the acid further produced from the acid generator by radiation irradiation, and controls the chemical reaction in a radiation non-irradiated light field which is not desirable. While the storage stability of a constituent improves and resolution improves as a resist by using such an acid diffusion control agent, line breadth change of the resist pattern by fluctuation of PED can be suppressed, and it becomes what was extremely excellent in process stability. As an acid diffusion control agent, the nitrogen-containing organic compound from which basicity changes neither with radiation irradiation nor BEKU is used preferably. As this nitrogen-containing organic compound, it is the following type (6), for example.

R10R11R12N ... (6)

Independently R10, R11, and R12 here, respectively A hydrogen atom, an alkyl group, the compound (it is hereafter called "a nitrogen-containing compound (I)"). in which an aryl group or an aralkyl radical is shown and which is come out of and expressed The diamino compound which has two nitrogen atoms in the same intramolecular (it is hereafter called "a nitrogen-containing compound (II)"). The poly amino polymer which has three or more nitrogen atoms (it is hereafter called "a nitrogen-containing compound (III)"). An amide group content compound, an urea compound, a nitrogen-containing heterocyclic compound, etc. can be mentioned.

[0054] As the above-mentioned nitrogen-containing compound (I), for example n-hexylamine, n-heptyl amine, Monoalkyl amines, such as n-octyl amine, n-nonyl amine, and n-DESHIRU amine; G n butylamine, G n-pentylamine, G n-hexylamine, a G n-heptyl amine, Dialkyl amines, such as a G n-octyl amine, a G n-nonyl amine, and a G n-DESHIRU amine; Triethylamine, Tree n propylamine, tree n butylamine, tree n-pentylamine, Tree n-hexylamine, a tree n-heptyl amine, a tree n-octyl amine, Alkylamine, such as a tree n-nonyl amine and a tree n-DESHIRU amine; An aniline, Aromatic amine, such as N-methylaniline, N,N-dimethylaniline, 2-methylaniline, 3-methylaniline, 4-methylaniline, 4-nitroaniline, a diphenylamine, a triphenylamine, and a naphthylamine, can be mentioned.

[0055] As the above-mentioned nitrogen-containing compound (II), for example Ethylenediamine, N and N, N', N'-tetramethylethylenediamine, Tetramethylenediamine, hexamethylenediamine, 4, and 4'-diamino diphenylmethane, A - diamino diphenyl ether, and 4 and 4 '4, 4'-diamino benzophenone, A - diamino diphenylamine, and 4 and 4 '2, 2'-bis(4-aminophenyl) propane, A

2-(3-aminophenyl)-2-(4-aminophenyl) propane, A 2-(4-aminophenyl)-2-(3-hydroxyphenyl) propane, 2-(4-aminophenyl)-2-(4-hydroxyphenyl) propane, 1, and 4-bis[1-(4-aminophenyl)-1-methylethyl] benzene, 1, and 3-bis[1-(4-aminophenyl)-1-methylethyl] benzene etc. can be mentioned.

[0056] As the above-mentioned nitrogen-containing compound (III), the polymer of polyethyleneimine, the poly allylamine, and dimethylaminoethyl acrylamide etc. can be mentioned, for example. As the above-mentioned amide group content compound, a formamide, N-methyl formamide, N,N-dimethylformamide, an acetamide, N-methyl acetamide, N,N-dimethylacetamide, a propione amide, a benzamide, a pyrrolidone, N-methyl pyrrolidone, etc. can be mentioned, for example. As the above-mentioned urea compound, urea, methyl urea, 1, and 1-dimethylurea, 1, 3-dimethylurea, 1, 1 and 3, 3-tetramethyl urea, 1, 3-diphenyl urea, tributyl thiourea, etc. can be mentioned, for example.

[0057] As the above-mentioned nitrogen-containing heterocyclic compound, for example An imidazole, benzimidazole Imidazole derivatives, such as 4-methyl imidazole and 4-methyl-2-phenylimidazole; A pyridine, 2-methylpyridine, 4-methylpyridine, 2-ethylpyridine, 4-ethyl pyridine, 2-phenyl pyridine, 4-phenyl pyridine, an N-methyl-4-phenyl pyridine, Nicotine, a nicotinic acid, nicotinamide, a quinoline, 8-oxyquinoline, Pyrazine besides pyridines, such as an acridine, a pyrazole, pyridazine, Kino ZARIN, pudding, pyrrolidine, piperidine, morpholine, 4-methyl morpholine, piperazine, 1, 4-dimethyl piperazine, 1, and 4-diazabicyclo [2.2.2] octane etc. can be mentioned. A nitrogen-containing compound (I), a nitrogen-containing heterocyclic compound, etc. are desirable among these nitrogen-containing organic compounds. Moreover, especially in a nitrogen-containing compound (I), alkylamine is desirable, and pyridines are desirable especially in a nitrogen-containing heterocyclic compound.

[0058] In this invention, an acid diffusion control agent is independent, or can mix and use two or more sorts. The amount of the acid diffusion control agent used in this invention is usually 0.005 – 5 weight section preferably [it is desirable and] to 0.001 – 10 weight section and a pan below 15 weight sections per sum total weight 100 weight section of a copolymer (A) and (B). In this case, when the amount of the acid diffusion control agent used exceeds 15 weight sections, there is an inclination for the development nature of the sensibility as a resist or the exposure section to fall. In addition, there is a possibility that the pattern configuration and dimension fidelity as a resist may fall [the amount of the acid diffusion control agent used] depending on process conditions under in the 0.001 weight section.

[0059] In alkali fusibility resin this invention, if needed, it is resin other than a copolymer (A) and a copolymer (B), and the resin of alkali fusibility can be added. The resin of this alkali fusibility is resin meltable to an alkali developer which has one or more sorts of acid functional groups, such as the functional group which shows an alkali developer and compatibility, for example, a phenolic hydroxyl group, and a carboxyl group. As a result of control of the dissolution rate to the alkali developer of the resist coat by this invention constituent becoming easier by using such alkali fusibility resin, development nature can be raised further.

[0060] Although it is not limited especially as long as such alkali fusibility resin is meltable to an alkali developer, as desirable alkali fusibility resin For example, hydroxystyrene, an isopropenyl phenol, a

vinyl benzoic acid, Carboxy methyl styrene, carboxy methoxy styrene, an acrylic acid (meta), A crotonic acid, a maleic acid, a fumaric acid, an itaconic acid, citraconic acid Mesaconic acid, The addition polymerization system resin containing the repeating unit to which the polymerization nature double bond part of at least one sort of monomers which have acid functional groups, such as a cinnamic acid, cleft, the polycondensation system resin containing the condensed system repeating unit which has the acid functional group represented by novolak resin, etc. can be mentioned.

[0061] Although the alkali fusibility resin which consists of said addition polymerization system resin may consist of only repeating units to which the polymerization nature double bond part of the monomer which has said acid functional group cleft, as long as the generated resin is meltable to an alkali developer, it can also contain further one or more sorts of other repeating units. As such other repeating units, for example Styrene, alpha methyl styrene, Vinyltoluene, a maleic anhydride, acrylonitrile (meta), croton nitril, Mallein nitril, fumaronitrile, mesa KONNITORIRU, SHITORAKONNITORIRU, ITAKON nitril, acrylamide (meta), a croton amide, a mallein amide, A fumaric amide, mesa KONAMIDO, SHITORAKONAMIDO, an ITAKON amide, The repeating unit to which the polymerization nature double bond part of monomers, such as a vinyl aniline, vinylpyridine, N-vinyl-epsilon caprolactam, N-vinyl pyrrolidone, and N-vinyl imidazole, cleft can be mentioned.

[0062] The permeability of the radiation when considering as a resist coat among said addition polymerization system resin is high, and especially Pori (hydroxystyrene) and Pori (isopropenyl phenol) are desirable from a viewpoint of excelling also in dry etching resistance. Moreover, although the alkali fusibility resin which consists of said polycondensation system resin may consist of only polycondensation system repeating units which have an acid functional group, as long as the generated resin is meltable to an alkali developer, it can also contain other repeating units further. Such polycondensation system resin can be manufactured by carrying out the polycondensation (**) of one or more sorts of phenols, and one or more sorts of aldehydes under existence of an acid catalyst or a basic catalyst and in a water medium or the mixed medium of water and a hydrophilic solvent with the polycondensation component which can form other polycondensation system repeating units by the case.

[0063] As said phenols, for example o-cresol, m-cresol, P-cresol, 2, 3-xyleneol, 2, 4-xyleneol, 2, 5-xyleneol, 3, 4-xyleneol, 3,5-xyleneol, 2 and 3, a 5-trimethyl phenol, 3 and 4, a 5-trimethyl phenol, etc. can be mentioned. As said aldehydes For example, formaldehyde, a trioxane, a paraformaldehyde, a benzaldehyde, an acetaldehyde, a propyl aldehyde, phenylacetaldehyde, etc. can be mentioned. The amount of the alkali fusibility resin used in this invention is usually below the 200 weight sections per a total of 100 weight sections of said copolymer (A) and copolymer (B).

[0064] In a surfactant this invention constituent, as this surfactant that can add a surfactant The polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, The polyoxyethylene oleyl ether, the polyoxyethylene octyl phenol ether, The polyoxyethylene nonyl phenol ether, a polyethylene-glycol JIRAU rate, and polyethylene-glycol distearate can be mentioned. As a commercial item For example, EFUTOPPU EF301, EF303, and EF352 (product made from TOKEMU products), Megger facsimile F171, F173 (Dainippon Ink make), Fluorad FC430 and FC431 (Sumitomo 3M make), the

Asahi guard AG710, Sir chlorofluorocarbon S-382, SC101, SC102, SC103, SC104, SC105, SC106 (Asahi Glass Co., Ltd. make), Poly flow No.75 which are organosiloxane polymer KP341 (Shin-Etsu Chemical Co., Ltd. make), an acrylic-acid system, or a methacrylic-acid system (**) polymer, No.95 (a trade name, product made from Kyoeisha Fats-and-oils Chemical industry), etc. are used.

[0065] The loadings of a surfactant are usually below 2 weight sections per total quantity 100 weight section of a copolymer (A) and a copolymer (B).

[0066] A sensitizer can be added in a sensitizer this invention constituent. This sensitizer absorbs the energy of a radiation, transmits that energy to a radiation-sensitive acid generator, shows the operation which makes the amount of generation of an acid increase by that cause, and has the effectiveness of raising the sensibility of the appearance of the resist formed with this invention constituent. Benzophenones, roses bengal, anthracene, etc. can be mentioned as an example of a desirable sensitizer. The loadings of these sensitizers are usually below 50 weight sections per a total of 100 weight sections of the copolymer in a constituent (A), and a copolymer (B).

[0067] By blending a color and/or a pigment, other additive this invention constituents can make the latent image of the radiation irradiation section able to visualize, can ease the effect of the halation at the time of radiation irradiation, and can improve an adhesive property with a substrate further by blending an adhesion assistant. Furthermore, antihalation agents, such as a 4-hydroxy-4'-methyl chalcone, a configuration amelioration agent, a preservation stabilizer, a defoaming agent, etc. can also be blended as other additives.

[0068] On the occasion of the activity, a solvent this invention constituent is prepared as a constituent solution, when the concentration of total solids filters with the filter of about 0.2 micrometers of apertures after dissolving in a solvent five to 50% of the weight at homogeneity so that it may become 15 - 40% of the weight preferably for example.

[0069] As a solvent used for preparation of said constituent solution For example, ethylene glycol monoalkyl ether acetate, such as ethylene glycol monomethyl ether acetate and ethylene glycol monoethyl ether acetate; Propylene glycol monomethyl ether, The propylene glycol monoethyl ether, the propylene glycol monopropyl ether, Propylene glycol monoalkyl ether, such as the propylene glycol monobutyl ether; Propylene glycol wood ether, Propylene glycol dialkyl ether, such as propylene glycol diethylether, propylene glycol dipropyl ether, and propylene glycol dibutyl ether;

[0070] Propylene-glycol-monomethyl-ether acetate, propylene glycol monoethyl ether acetate, Propylene glycol monoalkyl ether acetate, such as propylene glycol monopropylether acetate and propylene glycol monobutyl ether acetate; Methyl lactate, Lactate, such as ethyl lactate, lactic-acid n-propyl, and lactic-acid isopropyl; Formic-acid n-amyl, Aliphatic series carboxylate, such as isoamyl formate, ethyl acetate, n-propyl acetate, isopropyl acetate, n-butyl acetate, isobutyl acetate, n-amyl acetate, isoamyl acetate, propionic-acid isopropyl, propionic-acid n-butyl, and propionic-acid isobutyl;

[0071] Hydroxyacetic acid ethyl, 2-hydroxy-2-methyl ethyl propionate, 2-hydroxy-3-methyl methyl butyrate, methoxy ethyl acetate, ethoxy ethyl acetate, 3-methoxy methyl propionate, 3-methoxy ethyl propionate, 3-ethoxy methyl propionate, 3-ethoxy ethyl propionate, 3-methoxy butyl acetate, 3-methyl-3-methoxy butyl acetate, 3-methyl-3-methoxy butyl propionate,

3-methyl-3-methoxybutyl butyrate, Other ester, such as methyl acetoacetate, an ethyl acetoacetate, methyl pyruvate, and pyruvic-acid ethyl; Toluene, Aromatic hydrocarbon, such as a xylene; A methyl ethyl ketone, methyl propyl ketone, Methyl butyl ketone, 2-heptanone, 3-heptanone, 4-heptanone, Ketones, such as a cyclohexanone; lactone [, such as amides; gamma-butyrolactone,], such as N-methyl formamide, N.N-dimethylformamide, N-methyl acetamide, N,N-dimethylacetamide, and N-methyl pyrrolidone, can be mentioned.

[0072] In case a resist pattern is formed from the formation this invention constituent of a resist pattern As it mentioned above, the prepared constituent solution with proper spreading means, such as revolution spreading, flow casting spreading, and roll coating For example, by applying on substrates, such as a silicon wafer and a wafer covered with aluminum, a resist coat is formed and it heat-treats beforehand by the case (it is hereafter called "prebake"). After carrying out, radiation irradiation (henceforth "exposure") is carried out through a predetermined mask pattern. As a radiation used in that case, charged-particle lines [, such as an X-ray; electron ray,], such as far-ultraviolet-rays; synchrotron radiation lines, such as ultraviolet-rays;ArF excimer lasers (wavelength of 193nm), such as i line (wavelength of 365nm), and a KrF excimer laser (wavelength of 248nm), are used, choosing them suitably, corresponding to the class of radiation-sensitive acid generator. Moreover, exposure conditions, such as light exposure, are suitably selected according to the combination presentation of this invention constituent, the class of each additive, etc.

[0073] In this invention, in order to raise the sensibility of the appearance of a resist coat, it is desirable to heat-treat after exposure (henceforth "BEKU after exposure"). Although the heating condition changes according to the combination presentation of this invention constituent, the class of each additive, etc., it is usually 40-150 degrees C preferably 30-200 degrees C. Subsequently, a predetermined resist pattern is formed by usually carrying out alkali development of the exposed resist coat with an alkali developer on 10-50 degrees C and the conditions for 30 - 200 seconds.

[0074] As said alkali developer, for example Alkali-metal hydroxide; aqueous ammonia; Monod, G or the Tori-alkylamines; Monod, G or Tori-alkanolamine; heterocyclic amine; tetrapod alkylammonium hydroxide; choline;1, 8-diazabicyclo-[5.4.0]-7-undecene, The alkaline water solution which usually dissolved alkaline compounds, such as 1 and 5-diazabicyclo-[4.3.0]-5-nonene, one to 10% of the weight so that it might become 1 - 5% of the weight of concentration preferably is used. Moreover, to the developer which consists of said alkaline water solution, water-soluble organic solvents and surfactants, such as a methanol and ethanol, can also be added suitably. And in using the developer which consists of an alkaline water solution in this way, generally it rinses after development. In addition, since the effect of the basic impurity contained in an environmental ambient atmosphere is prevented on the occasion of formation of a resist pattern, a protective coat can also be prepared on a resist coat.

[0075]

[Example] Hereafter, an example and the example of a comparison are given and this invention is explained still more concretely. However, this invention is not restrained at all by these examples. Here, measurement of Mw and assessment of each resist were performed in the following way.

[0076] It measured using the GPC column (two G2000HXL(s), one G3000HXL, and one G4000HXL)

by Mw TOSOH CORP. with the gel permeation chromatography which makes mono dispersion polystyrene a criterion on analysis conditions with a flow rate tetrahydrofuran [a part for /and the elution solvent tetrahydrofuran of 1.0ml], and a column temperature of 40 degrees C.

[0077] Light exposure which forms line - and - tooth-space pattern (1L1S) with a line breadth [when forming a sensibility resist pattern] of 0.3 micrometers in the line breadth of 1 to 1 was made into the optimal light exposure, and this optimal light exposure estimated sensibility.

[0078] The lower limit (micrometer) of the resist pattern resolved when it exposes with the resolution optimal light exposure was made into resolution.

[0079] In line - and - tooth-space pattern with a pattern configuration of 0.3 micrometers, the time of the round top and $La \geq 1.1 \times Lb$ was expressed [the time of $0.9 \times Lb < La < 1.1 \times Lb$] for the time of fitness and $0.9 \times Lb \geq La$ as a T-mold, having used line breadth of La and the pattern lower part as Lb for the line breadth of the pattern upper part.

[0080] The resist coat of a development nature constituent was formed and Society for Cutting Up Men after pattern formation and extent of the development remainder were investigated using the scanning electron microscope.

The preservation stability constituent was prepared, and the sensibility after three-week preservation was measured and investigated by the sensibility immediately after preparation, and 35-degree-C preservation.

[0081] After dissolving example of synthetic composition 1 Pori (p-hydroxystyrene) (Mw12,000) 24g of a copolymer (A) in 100ml of dioxanes, nitrogen performed bubbling for 30 minutes. It added in this solution and 1g of p-toluenesulfonic-acid pyridinium salt was made to react to it as ethyl-vinyl-ether 8g and a catalyst for 12 hours. This reaction solution was dropped at the aqueous ammonia solution 1% of the weight, and the copolymer was settled. This polymer was dried within the 50-degree C vacuum dryer overnight. Mw was 16,000 and the obtained copolymer was what has the structure where 45% of the hydrogen atom of a phenolic hydroxyl group was permuted by 1-ethoxyethyl radical, as a result of 13 C-NMR measurement. Let this copolymer be a polymer A-1.

[0082] After dissolving synthetic example 2 Pori (p-hydroxystyrene) (Mw8,000) 24g in 100ml of dioxanes, nitrogen performed bubbling for 30 minutes. It added in this solution and 0.4g of p-toluenesulfonic-acid pyridinium salt was made to react to it as 2 and 3-dihydropyran 7.5g and a catalyst for 6 hours. This reaction solution was dropped at the aqueous ammonia solution 1%, and the copolymer was settled. This copolymer was dried within the 50-degree C vacuum dryer overnight. Mw was 11,000 and the obtained copolymer was what has the structure where 42% of the hydrogen atom of a phenolic hydroxyl group was permuted by the tetrahydropyranyl group, as a result of 13 C-NMR measurement. Let this copolymer be a polymer A-2.

[0083] Each copolymer was compounded using the vinyl ether compound shown in the phenolic hydroxyl group content polymer and table 1 having shown in a table 1 like the synthetic example 3 - the example 1 of 6 composition. The analysis value of a copolymer is shown in a table 1. Let this copolymer be a polymer A-3 to A-5.

[0084]

[A table 1]

| 合成例 共重合体 | 合成例3 A-3 | 合成例4 A-4 | 合成例5 A-5 |
|----------------------------|--------------------------|--------------------------|--------------------------|
| フェノール性水酸基含有共重合体 (Mw) | ポリ-p-ヒドロキシスチレン 15,000 | ポリ-p-ヒドロキシスチレン 18,000 | ポリ-p-ヒドロキシスチレン 15,000 |
| ビニルエーテル化合物 | エチルビニルエーテル | エチルビニルエーテル | プロピルビニルエーテル |
| フェノール性水酸基の水素原子が 置換された構造 | 1-エトキシエチル基 | 1-エトキシエチル基 | 1-プロポキシエチル基 |
| フェノール性水酸基の置換率 (モル%) | 38 | 35 | 33 |
| Mw | 18,000 | 21,000 | 18,000 |

[0085] Example of synthetic composition 7p-acetoxy styrene 30g and styrene 10g of a copolymer (B) were mixed with dioxane 50g, and it considered as the homogeneity solution. The polymerization of the reaction temperature was maintained and carried out to 60 degrees C for 7 hours, adding 2 and 2'-azobis (4-methoxy-2,4-dimethylvaleronitrile) 1.9g, and continuing bubbling, after carrying out bubbling of this solution for 30 minutes with nitrogen. The reaction solution was mixed with a lot of hexanes after polymerization termination, and the generated copolymer was made to solidify. Subsequently, after remelting a copolymer to dioxane, again, by the hexane, the actuation made to solidify was repeated several times, the unreacted monomer was removed thoroughly, it dried under 50-degree-C reduced pressure, and the white copolymer was obtained. Subsequently, the copolymer was again dissolved in dioxane 100g, 20g of sulfuric-acid water was added 10%, and hydrolysis was performed at 80 degrees C for 6 hours. It put, after having added 100g of ethyl

acetate to the solution, adding 100g of distilled water subsequently and shaking, and the water layer was discarded. Then, rinsing was repeated until PH of a water layer became neutrality. Subsequently, the vacuum drying was solidified and carried out in a lot of hexanes, and white powder was obtained. Mw was 9,000 and the copolymerization mole ratio of p-hydroxystyrene and styrene of the obtained copolymer was 70:30 as a result of ¹H-NMR measurement. Let this copolymer be a polymer B-1.

[0086] A polymerization, clearance of an unreacted object, and acidolysis were performed for p-butoxy styrene 30g and styrene 5.3g like the example 7 of synthetic example 8 composition, Mw is 7,000 and the copolymerization mole ratio of hydroxystyrene and styrene obtained the copolymer of 80:20. Let this copolymer be a polymer B-2.

[0087] A polymerization, clearance of an unreacted object, and acidolysis were performed for p-butoxy styrene 28g and styrene 30g like the example 7 of synthetic example 9 composition, Mw is 7,000 and the copolymerization mole ratio of hydroxystyrene and styrene obtained the copolymer of 60:40. Let this copolymer be a polymer B-3.

[0088] After dissolving synthetic example 10 Pori (p-hydroxystyrene) (Mw8,000) 24g in 100ml of dioxanes, nitrogen performed bubbling for 30 minutes. Triethylamine 50g is added, and JI t-butyl dicarbonate 6.5g was added in this solution, and it was made to react to it at 5 degrees C under stirring for 6 hours. Then, this reaction solution was dropped at the aqueous ammonia solution 1% of the weight, and the copolymer was settled. This copolymer was dried within the 50-degree C vacuum dryer overnight. Mw was 11,000 and the obtained copolymer was what has the structure where 25% of the hydrogen atom of a phenolic hydroxyl group was permuted by the t-butoxycarbonyl group, as a result of ¹³C-NMR measurement. Let this copolymer be a polymer C-1.

[0089] After mixing each component shown in one to examples 1-10 and example of comparison 3 table 3 (however, the section is based on weight) and considering as a homogeneity solution, it filtered with the membrane filter of 0.2 micrometers of apertures, and the constituent solution was prepared. Then, after carrying out the spin coat of the class product solution on a silicon wafer, prebake was performed for 120 seconds at 90 degrees C, and the resist coat of 1.0 micrometers of thickness was formed. Subsequently, after exposing with the KrF excimer laser (stepper NSR[by NIKON CORP.]-2005EX8A is used) and performing BEKU after exposure for 60 seconds at 100 degrees C subsequently, paddle development was carried out for 1 minute at 23 degrees C using the tetramethylammonium hydroxide water solution 2.38% of the weight, it rinsed and dried with pure water, and the resist pattern was formed. The assessment result of each resist is shown in a table 4.

[0090]

[A table 2]

| | (A) 共重合体 (部) | (B) 共重合体 (部) | 共重合体(A)及び 共重合体(B)以外 の共重合体 (部) | (C) 酸発生剤 (部) | (D) 酸拡散制御剤 (部) | 溶 剤 (部) |
|------|--------------------|--------------------|-------------------------------------|--------------------|----------------------|-------------|
| 実施例1 | A-1(75) | B-1(25) | — | C-1(2) | イ(0.15) | PGMEA (400) |
| 実施例2 | A-1(75) | B-2(25) | — | C-2(4) | ロ(0.12) | PGMEA (400) |
| 実施例3 | A-2(80) | B-2(20) | — | C-3(6) | ロ(0.12) | MMP (400) |
| 実施例4 | A-2(80) | B-1(20) | — | C-3(6) | イ(0.15) | MMP (400) |
| 実施例5 | A-3(85) | B-2(15) | — | C-1(2) | ロ(0.12) | PGMEA (400) |
| 実施例6 | A-3(85) | B-1(15) | — | C-2(4) | イ(0.15) | PGMEA (400) |
| 実施例7 | A-4(65) | B-2(35) | — | C-3(6) | イ(0.15) | MMP (400) |
| 実施例8 | A-4(70) | B-2(30) | — | C-3(6) | ロ(0.12) | PGMEA (400) |
| 実施例9 | A-5(80) | B-2(20) | — | C-1(2) | イ(0.15) | EL (400) |
| 比較例1 | A-1(100) | — | — | C-1(2) | イ(0.15) | PGMEA (400) |
| 比較例2 | A-2(80) | — | C-1(20) | C-1(2) | イ(0.15) | PGMEA (400) |

[0091]

[A table 3]

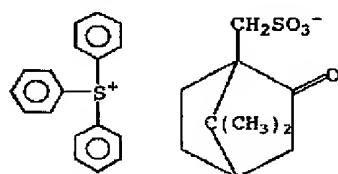
| | 感 度 (mJ/cm ²) | 解像度 (μm) | パターン形状 | 現像性 | 保存安定性 3週間後の感度 |
|------|------------------------------|-------------|--------|-----|------------------|
| 実施例1 | 20 | 0.20 | 良好 | 良好 | 20 |
| 実施例2 | 26 | 0.22 | 良好 | 良好 | 26 |
| 実施例3 | 29 | 0.22 | 良好 | 良好 | 29 |
| 実施例4 | 29 | 0.20 | 良好 | 良好 | 29 |
| 実施例5 | 21 | 0.22 | 良好 | 良好 | 21 |
| 実施例6 | 27 | 0.22 | 良好 | 良好 | 27 |
| 実施例7 | 29 | 0.20 | 良好 | 良好 | 29 |
| 実施例8 | 31 | 0.22 | 良好 | 良好 | 31 |
| 実施例9 | 20 | 0.22 | 良好 | 良好 | 20 |
| 比較例1 | 29 | 0.27 | 良好 | 劣有り | 29 |
| 比較例2 | 25 | 0.22 | 良好 | 良好 | 49 |

[0092] Here, the radiation-sensitive acid generator in each example and the example of a comparison, an acid diffusion control agent, and the solvent are as follows.

radiation-sensitive acid generator (acid generator) C-1:triphenylsulfonium trifluoromethane sulfonate -- C-2:triphenylsulfonium camphor sulfonate *C-3: -- bis(phenyl sulfonyl) cyclohexane *C-2 are a compound which has the following structure expression.

[0093]

[Formula 9]



[0094] acid diffusion control agent I: -- nicotinic-acid AMIDORO: -- Tori n butylamine [0095]

Solvent EL: Ethyl-lactate MMP:3-methoxy methyl-propionate PGMEA:

Propylene-glycol-monomethyl-ether acetate [0096]

[Effect of the Invention] Especially the radiation-sensitive constituent of this invention is excellent in sensibility, resolution, development nature, and a pattern configuration, and, moreover, excellent in

the preservation stability of sensibility. And the radiation-sensitive constituent of this invention responds effective in the various radiations like ultraviolet rays, far ultraviolet rays, an X-ray, or a charged-particle line, and is very useful as a chemistry magnification mold positive resist. Therefore, the radiation-sensitive constituent of this invention can be suitably used as an object for semiconductor device manufacture expected that detailed-ization will advance further from now on.

[Translation done.]